UCRL-99646
PREPRINT

Advanced Phosphate Glasses for High Average Power Lasers

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This paper was prepared for submittal to the proceedings of the International Congress on Optical Science and Engineering, Paris, France
April 24-28, 1989

July, 1989

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Advanced Phosphate glasses for high average power lasers*

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Abstract

Phosphate glass compositions with superior properties for operation as active elements in high average power lasers have been developed. Large, high optical quality castings of these new glasses that are free of metallic inclusions have been made by Schott Glass Technologies and by Hoya Optics. The laser requirements, glass development strategy, and the resultant laser and thermo-mechanical properties of the advanced phosphate glasses are analyzed.

1. Introduction

Phosphate glasses are popular as laser hosts due to their good laser properties arising from the advantageous site for neodymium substitution.[1] This gives a high stimulated emission cross section and relatively long radiative lifetime. While some hosts exist with slightly better laser properties, such as the fluorophosphates, phosphate glasses can be produced relatively inexpensively in large castings (10 liter) with outstanding optical homogeneity and free of damaging metallic inclusions.[2]

Compositional development of phosphate laser hosts has historically focused on optimizing the laser properties; by far the majority of the laser glass produced to date has been used in high peak power, single pulse lasers for inertial confinement fusion research. These glasses are generally potassium-barium-aluminum phosphates and have stimulated emission cross section values in excess of 4×10^{-20} cm^2.

The renewed interest in solid state lasers over the past several years has focused attention on appropriate hosts for operation at high average power. In such lasers a thermal gradient develops in the steady state in which the center of the amplifier element is at a higher temperature than the cooled surfaces, giving rise to tensile surface stresses. In some designs, the fracture of the laser element from these thermally-induced stresses is the primary limitation on performance. While crystalline laser hosts are preferred for some applications, primarily high repetition frequency lasers, glass hosts are preferred in low and moderate repetition frequency lasers with high pulse energy requirements. One chief limitation to the usefulness of the present glasses for high average power operation is the low repetition frequency required to prevent fracture, which is due to the poor thermo-mechanical properties of phosphate glasses.

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*Work performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

For high average power, the phosphate glasses do not at first seem very promising. Indeed, the metaphosphates have been investigated for their very low melting temperature[3] and their high thermal expansion, which might permit them to be used as glass-to-aluminum metal seals.[4] Furthermore, the chemical durability of many of these phosphates is not good. However, several factors motivated us to examine the possibility of substantial improvement in thermo-mechanical properties of phosphate laser hosts: (1) excellent spectroscopic and laser properties, particularly emission cross section and radiative lifetime at high dopant concentration; (2) the availability of technology for casting large optical quality pieces that are free of metallic inclusions, and (3) the prospects for strengthening by ion exchange. In the following sections we discuss the properties requirements, from a laser application perspective, and the developmental effort for advanced phosphate glass.

2. Materials Properties Requirements

The laser and optical properties required for glass lasers are discussed in detail elsewhere.[5,6] In this development program our main interest was to improve the thermo-mechanical properties of the phosphate glass to increase suitability for operation at high average power. Fracture limitations have been discussed previously and are briefly reviewed here.[5,7,8]

For rod geometries the temperature difference between the centerline and the barrel is given by

$$\Delta T = P_V/4\pi\kappa L \tag{1}$$

where P_V is the thermal power per unit volume, L is the rod length, and κ is the thermal conductivity. For an assumed uniform disposition in the rod volume, V,

$$P_V = P_L f_Q/V \tag{2}$$

where P_L is the flashlamp power, and f_Q is the fraction of the flashlamp power that must be dissipated as heat in the rod. For materials with non-zero thermal expansion, α, this temperature difference gives rise to a strain

$$\varepsilon = \frac{\alpha\Delta T}{2(1-\nu)} \tag{3}$$

where ν is Poisson's ratio.

Substitution of the ratio of stress and strain, Young's modulus, E, gives the stress, σ, on the rod surface. For most materials which expand during heating, this stress is tensile at the cooled rod surface and must be less than the strength, σ_f, to prevent fracture.

$$\sigma_f > \sigma = \frac{\alpha E T}{2(1-\nu)} \tag{4a}$$

$$= \frac{\alpha E P_L f_Q}{8\pi^2(1-\nu)kL^2r^2} \tag{4b}$$

where r is the rod diameter.

For rectangular slab geometries, a similar one-dimensional analysis[7] based on a uniformly pumped infinite flat plate, gives

$$\sigma = 2\alpha\Delta TE/3(1-\nu)$$

$$= \frac{P_L f_Q tE\alpha}{12kw\ell(1-\nu)} \tag{5}$$

where t, w, and ℓ are the slab thickness, width, and length, respectively. We note that heating and cooling non-uniformities and edge effects can give localized concentration of the stress estimated by Eq. (5) resulting in fracture at low values.

With regard to the development aspects of these materials; expressions (4) and (5) can be rearranged, grouping the materials properties as

$$\sigma_{rod} = \frac{P_L f_Q b}{8\pi^2 L^2 r^2} \left[\frac{E\alpha}{\sigma_f \kappa(1-\nu)}\right] \tag{6}$$

$$\sigma_{slab}^{1-D} = \frac{P_L f_Q tb}{12w\ell} \left[\frac{E\alpha}{\sigma_f \kappa(1-\nu)}\right] \tag{7}$$

where

$$R_T = \frac{\sigma_f \kappa(1-\nu)}{\alpha E} \tag{8}$$

R_T is the thermal stress resistance figure of merit[5,8] (FOM) and b is the fracture ratio, the ratio of stress to strength.

The thermal stress resistance parameter R_T contains intrinsic materials properties except strength, which depends on both the intrinsic strength of the material, as well as the defects in the material. These defects typically limit the strength of components fabricated from brittle materials to about 10^{-3} of their theoretical, defect-free state.

It has been recognized that since the strength of seemingly similarly prepared optical surfaces may vary by 10x or more,[9] two versions of R_T are required[8]. R_T, Eq. (8) is appropriate for use in laser design where the strength, σ_f, of the component has been characterized, for example, by Weibull analysis.[7] On the other hand, for comparing one material with another, R_T is re-expressed using all intrinsic parameters, replacing the component strength σ_f, by K_c, the fracture toughness. K_c is a measure of the material's inherent resistance to crack propagation. The intrinsic thermal stress resistance parameter[8]

$$R_T^* = \frac{K_c \kappa (1-\nu)}{\alpha E} \tag{9}$$

is used to characterize new materials and to compare various materials with regard to their thermal stress resistance.

3. Glass Development

Under contract to LLNL, and with internal funding, Hoya Corp.,[10] Schott Glass Technologies,[11] and Hoya Optics,[12] have developed several new glasses with substantially improved thermo-mechanical properties, and with concurrent good laser properties (Table 1).

Table 1. Improvements in thermo-mechanical properties of advanced phosphate laser glasses

	High cross-section phosphate glasses (LHG-8, LG-750)	Advanced phosphate glasses (APG-1, HAP-4)
R_T, $W/m^{-1/2}$	0.28	0.73
$\sigma_e \times 10^{-20}$ cm^2	4.0	3.5
τ_3, μsec (3% Nd)	350	330
$R_T\ \sigma_e \tau_3$	390	840

LG-750, APG-1: Schott Glass Technologies

LHG-8, HAP-4: Hoya Optics

Within measurement accuracy, these glasses appear to have essentially identical properties--about 2x better than previous platinum inclusion-free glasses.

The development focused on simultaneously satisfying good thermo- mechanical and laser properties, adequate chemical durability, and adequate platinum solubility rate to permit melting of inclusion-free castings. Additionally, compositions with small alkali ions amenable to ion exchange strengthening were favored. Based on previous work, summarized in Ref. 1, we examined the cation/modifier role in determining combined laser and thermo-mechanical properties. We use a combined thermo-mechanical/laser properties figure of merit, [$R_T^* \sigma_e \tau_3$], where σ_e is the cross section for stimulated emission, and τ_3 is the radiative lifetime at 3% Nd. Examining the relationship for meta- and ultra-phosphates between this FOM [$R_T^* \sigma_e \tau_3$] and the cation strength of the modifier ions (Z^2/a) where Z is the atomic number and a is the ionic radius immediately directs development to lithium-substituted glasses (Figure 1)[13].

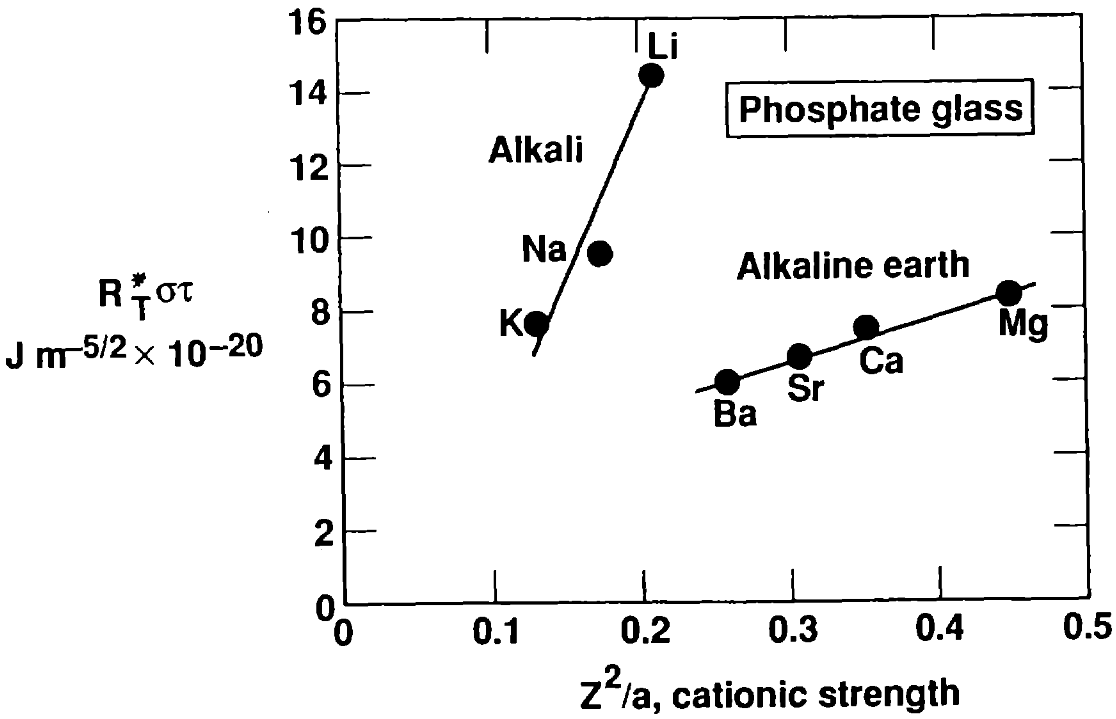

Figure 1. The modifier ion effect on the thermo-mechanical laser properties of meta- and ultra-phosphate laser glasses. R_T^* is the intrinsic thermal stress resistance parameter, σ is the stimulated emission cross section and τ is the radiative lifetime at 3% Nd.

Also, this is advantageous for ion exchange, since the small lithium ions can be readily leached from the surface and replaced with larger Na or K ions in $NaNO_3/KNO_3$ salts baths. The resultant compressive surface layer results in substantial strengthening.[14]

Issues of durability, melt temperature and viscosity, glass stability and Pt solubility rate were resolved by minor additions of alumina other cations, and specific property ingredients. The result is that both Schott Glass Technologies' Advanced Phosphate Glass, APG-1, and Hoya Optics, Inc.'s High Average Power glass, HAP-4, can be melted in large castings free of metallic inclusions with exceptional homogeneity. Initial ion exchange results[12,14] indicate that moderate stress (100-200 MPa) can be induced to adequate depth (20-50 microns) permitting substantial strengthening. The [$R_T^* \sigma_e \tau_3$] FOM is about 2x greater for these glasses than previous Pt-free compositions. Ion exchange, yet to be demonstrated for these compositions on large slabs, would increase [$R_T\sigma_e\tau_3$] by an additional ~4x, making these glasses nearly ten-fold better than their predecessors.

4. Acknowledgments

The author acknowledges the contributions of J. S. Hayden and D. L. Sapak, Schott Glass Technologies, Duryea, PA; H. Toratani, H. E. Meissner and H. C. Lee, Hoya Optics, Inc., Fremont, CA; T. Izumitani, Hoya, Inc. Tokyo, Japan; S. E. Stokowski, Tencor, Mountain View, CA; J. L. Emmett, JLE Associates, Pleasanton, CA; and A. J. Pertica, M. A. Summers and W. L. Gagnon, Lawrence Livermore National Laboratory.

5. References

1. S. E. Stokowski, Laser Glass: an Engineered Material, Lawrence Livermore National Laboratory, UCRL-96331, 1987.

2. J. S. Hayden, D. L. Sapak, and A. J. Marker, "Elimination of Metallic Platinum in Phosphate Laser Glasses," Proc. SPIE 895 (1988) and T. Izumitani, M. Matsukawa, and H. Miyade, "Solubility of Pt in Nd Phosphate Glass," NIST Spec. Publ. 756, 29 (1987).

3. N. H. Ray, et al., "Oxide Glasses of Very Low Softening Point," Part 1 Glass Techn. 14, 50 (1973).

4. J. A. Wilder, Jr., "Glasses and Glass Ceramics for Sealing Aluminum Alloys," J. Non-Cryst. Solids 38, 879 (1980).

5. J. L. Emmett, W. F. Krupke, and J. B. Trenholme, "Future Development of High Power Solid State Laser Systems," Sov. J. Quant. Electron. 13, 1 (1983).

6. J. E. Marion and A. J. Pertica, "Materials for High Average Power Lasers," SPIE, Proc. 1040, Los Angeles (1989).

7. J. E. Marion, "Fracture of Solid State Laser Slabs," J. Appl. Phys. 60, 69 (1986).

8. J. E. Marion, "Appropriate Use of the Strength Parameter in Solid State Laser Design," J. Appl. Phys. 62, 1595 (1987).

9. J. E. Marion, "Strengthened Solid State Laser Materials," Appl. Phys. Lett. 47, 694 (1985).

10. T. Izumitani, M. Matsukawa, C. Hata, K. Tanaka, and H. Toratani, "Development of Silicophosphate Glass, HAP-3," NIST Publ. 752, Boulder Damage Conf., 13 (1986).

11. J. S. Hayden, D. L. Sapak, and H. J. Hoffman, "Advances in Glasses for High Average Power Laser Systems," SPIE 1012, 36 (1988).

12. H. E. Meissner, H. Toratani, private communciation, Hoya Optics, Fremont, CA, 1988, 1989. HAP-3 was developed at Hoya, Inc., Tokyo, Japan, by T. Izumitani and coworkers. HAP-4 was developed at Hoya Optics, Fremont, by H. Toratani and coworkers.

13. J. E. Marion, Technical Information Seminar, Lawrence Livermore National Laboratory, November 1988.

14. H. Toratani, H. C. Lee, H. E. Meissner, and J. E. Marion, "Ion-exchanged Strengthened Laser Glass Slabs," Conference on Lasers and Electro Optics," Anaheim, CA, April 1988.